Catalytic Hydrogenolysis of Aromatic Halides with Sodium Hydride of Nanometric Size

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Aromatic halides, such as chlorobenzene and fluorobenzene, can be rapidly hydrodehalogenated in 100% conversion by sodium hydride of nanometric size in the presence of a multimetallic catalyst ($Ni(OAc)_2$–$TiCl_4$–*i*-PrONa).

The reduction of organic halides from aromatic ring is important in organic synthesis and environmental decontamination. The importance of this process has stimulated considerable investigations.[1-11] A number of approaches have been reported, especially with metal hydrides activated by transition metal salts;[1-6] however, most of the activating reagents for this process must be present in stoichiometric amount. Furthermore, the hydrodehalogenation of chloroarenes and fluoroarenes is still a difficult task because of their high bond dissociation energies. Recently, we have reported an easy method for the synthesis of sodium hydride of nanometric size (NaH*) by the catalytic method under mild conditions (average particle size: 23 nm, specific surface area: 90 m^2/g).[12] For a reaction concerned with the solid surface, the reaction rate might be increased by orders of magnitude when the nanomaterials are used instead of the usual commercial ones because the difference of the specific surface area between these two materials is around 2-3 orders of magnitude. This NaH* is very reactive toward many reactions which are difficult to proceed with the commercial ones.[12,13] In this letter, we report the use of NaH* for the hydrodehalogenation of aromatic halides in the presence of a catalyst. Some of the experimental results are summarized in Table 1. Under the reaction conditions indicated in Table 1, the commercial sodium hydride (Serva, average particle size ca. 2.5 μm) is practically inert to the reduction of chlorobenzene and the reaction rate is too slow to be measured, while NaH* gives 19% conversion in 2 h. The activity of NaH* can be promoted by a transition metal compound as catalyst. We have investigated many transition metal salts to increase the reducing ability of NaH* and found that VCl_3, $CoCl_2$, $NiCl_2$, $Ni(OAc)_2$, Cp_2TiCl_2 and $TiCl_4$ were efficient catalysts, among which, $Ni(OAc)_2$ was the most efficient one. In order to raise the reducing activity still further, attempts were made by combining two transition metal salts as catalyst.[14] For the sake of comparison, the total amount of the transition metal compound added was kept constant. As a result, a remarkable synergic effect has been observed, especially when a combination of $TiCl_4$ (or Cp_2TiCl_2) and $Ni(OAc)_2$ was used as catalyst, which led to a 100% conversion for the reduction of chlorobenzene in 2 h, whereas $Ni(OAc)_2$, Cp_2TiCl_2 or $TiCl_4$ itself gave only 64%, 56% and 55% conversion respectively under the same conditions. It can be seen from Table 1 that the same synergic effect can be observed in the reduction of *p*-fluorotoluene. Caubère *et al.* have reported that the reducing properties of commercial sodium hydride could be increased by the presence of a stoichiometric amount of metal salt and sodium alcoholate respect to substrate.[1] In our case, an addition of a catalytic amount of sodium isopropylate can increase the reducing property of NaH* further, and 100% conversion is obtained in 5 h, although sodium isopropylate alone is not a promoter for the reduction of aromatic halides with NaH*. In order to simplify the experimental procedure and utilize the catalyst $TiCl_4$ in the preparation of NaH*, a catalytic amount of nickel acetate and sodium isopropylate was added directly to the freshly prepared sodium hydride slurry[15] to form the complex reducing agent. Results are summarized in Table 2 for the reduction of aromatic halides. Table 2 shows that the complex reducing reagent freshly prepared in slurry is more effective than its powder form for the reduction of aromatic halides, especially for aromatic fluorides which is usually very difficult to proceed by other methods. The order of ease of reduction of aryl halides conforms to that of the usual reductive dehalogenation of organic halides. *i.e.* Br>Cl>>F. Most surprising is the rate of reduction of fluoroarenes to yield 100% conversion in a very short time. For example, the reduction of fluorobenzene gives 100% conversion only in 2 h. For three isomers of fluorotoluene, 3-4 h is needed for the complete hydrodefluorination. In addition to its high reactivity, this complex reducing reagent exhibits very good selectivity for the hydrodehalogenation of aromatic halides. In all of our experiments, no byproducts such as the coupling product *etc.* have been detected except the product of hydrodehalogenation.

Table 1. Reduction of chlorobenzene and *p*-fluorotoluene with sodium hydride powders of nanometric size using transition metal salts as catalyst in refluxing THF

Substrate	Catalyst (mole ratio of cat/NaH*)	Conversion (%)[c]
Chlorobenzene[a]	–	19
	$Cp_2TiCl_2(0.03)$	56
	$TiCl_4(0.03)$	55
	$VCl_3(0.03)$	45
	$CoCl_2(0.03)$	51
	$NiCl_2(0.03)$	60
	$Ni(OAc)_2(0.03)$	64
	$CoCl_2(0.015)+VCl_3(0.015)$	65
	$Cp_2TiCl_2(0.015)+VCl_3(0.015)$	51
	$Cp_2TiCl_2(0.015)+CoCl_2(0.015)$	49
	$Ni(OAc)_2(0.015)+CoCl_2(0.015)$	57
	$Ni(OAc)_2(0.015)+VCl_3(0.015)$	87
	$Ni(OAc)_2(0.015)+Cp_2TiCl_2(0.015)$	100
	$Ni(OAc)_2(0.015)+TiCl_4(0.015)$	100
p-Fluorotoluene[b]	$Ni(OAc)_2(0.03)$	27
	$Ni(OAc)_2(0.015)$ $+TiCl_4(0.015)$	38
	$Ni(OAc)_2(0.03)+$*i*-PrONa(0.075)	93
	$Ni(OAc)_2(0.015)$ $+TiCl_4(0.015)$ +*i*-PrONa(0.075)	100

Reaction conditions: THF 15mL, NaH 10 mmol, [a] NaH/transition metal salt/chlorobenzene = 2/0.06/1, 2h, temperature,66 °C. [b] NaH/transition metal salt/*p*-fluorotoluene = 3/0.09/1, 5 h. [c] Determined by GC analysis and benzene or toluene is the only product.

Table 2. Reduction of aromatic halides with sodium hydride slurry[15] (containing Ti species) of nanometric size in the presence of a catalytic amount of $Ni(OAc)_2$ and *i*-PrONa in refluxing THF

Substrate	Reaction time (h)	Conversion (%)^a	Product (%)^a
Bromobenzene	0.17	100	benzene(100)
Chlorobenzene	0.33	100	benzene(100)
Fluorobenzene	2	100	benzene(100)
p–Fluorotoluene	3	100	toluene(100)
m–Fluorotoluene	3	100	toluene(100)
o–Fluorotoluene	4	100	toluene(100)

Reaction conditions: NaH* slurry, containing 20 mmol NaH* and 0.3 mmol Ti(0) species, $Ni(OAc)_2$ 0.3 mmol, *i*-PrONa 1.5 mmol, NaH/substrate = 2, THF 15 mL, 66 °C. a. Determined by GC analysis.

In conclusion, by utilizing sodium hydride of nanometric size and the synergic effect of multimetallic catalyst, we obtain a highly reactive complex reducing reagent, which gives 100% hydrodehalogenation yield for the reduction of aromatic halides in a very short reaction time. It is a facile method for the reduction of aromatic halides, especially for chlorides and fluorides. The preliminary experimental results reveal that this complex reducing reagent is also efficient for the hydrogenolysis of alkyl halides and shows potential application in the reduction of nitro compounds, aldehydes and ketones. More detailed studies are in progress.

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References and Notes

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15 Preparation of the sodium hydride of nanometric size: 20 mmol of metallic sodium and 1 mmol of naphthalene were placed in a dry reaction vessel, 15 mL of tetrahydrofuran and 0.3 mmol $TiCl_4$ were added under argon. The argon was evacuated and hydrogen was passed into the reaction vessel. The uptake of hydrogen was measured with a constant-pressure gas burette. The reaction was maintained at 40 °C in an oil bath and the reaction mixture was stirred magnetically. After reaction was completed, a sodium hydride slurry containing Ti species was obtained. The prepared sodium hydride slurry was centrifuged and the solids were washed three times with THF and then evacuated at 60 °C to dryness. The NaH* powder was obtained.